

Potential Dilemma: The Methods of Meeting Automotive Exhaust Emission Standards of the Clean Air Act of 1970

by Warren T. Piver *

This review attempts to provide an overview of the interconnected industrial changes associated with compliance with the exhaust emission standards of the Clean Air Act of 1970. To understand the complex nature of air pollution problems, Federal legislation, and compliance with this legislation requires an understanding of automotive technology, petroleum refining, atmospheric chemistry and physics, economics, and public health. The endeavors of all of these different areas impinge to a greater or lesser extent on the final response to the Clean Air Act which is designed to safeguard public health.

This overview begins by examining gasoline refinery practice and gasoline composition. Included in this discussion are average values for trace contaminants in gasoline, and an explanation of the function of the many gasoline additives. Next, exhaust emissions are characterized, average values of exhaust components given, and a summary of important atmospheric air pollution reactions presented. Emission control devices and sulfate emissions from these devices are described. This is followed by a complete discussion of methyl cyclopentadienyl manganese tricarbonyl, a substitute antiknock for tetraethyllead. In the event TEL is legally banned from gasoline, or removed because it poisons the catalytic muffler surface, this manganese antiknock is the most efficacious replacement. In this discussion, the adverse health effects caused by exposure to manganese oxide particulates, the possible exhaust emission products from this additive, are examined in detail. The review concludes with comments on automotive engine and gasoline composition redesign as an approach to automotive air pollution.

Introduction and Background

In 1952, Hagen-Smit (1) demonstrated that smog in Los Angeles was formed from two automotive exhaust gas pollutants, unburned

hydrocarbons and nitric oxides. In effect, this study first showed clearly that the automobile, which had become an integral part of American culture, was a public health problem. The irony of this was that the turn-of-the-century expectations for the automobile foresaw it as a solution to many of the public health problems engendered by the horse and carriage (2). Some selected expectations were reduction of city

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noise, restoration of frayed nerves, relief of traffic congestion, increased economy of operation, and the reduction of population movement from rural to urban areas. In effect, the study by Hagen-Smit stimulated much concern, debate, raised blood pressures, Federal agency creation, and pressure by different interest groups as to what other pollutants were present in automotive exhaust, what effect they had on the environment, and what could be done to remove the source of these pollutants. The combustion of leaded gasoline in the spark-ignited automotive engine, in particular was identified as the major mobile source of hydrocarbons, carbon monoxide, nitrogen oxides, lead halide particulates, and other particulate matter. Presently, there are about 90 million passenger cars in operation which use about 10^{11} gal gasoline/yr. In 1968, 75 million cars produced 128×10^9 lb of CO, 34×10^9 lb of hydrocarbons, and 16×10^9 lb of nitrogen oxides (3).

A portion of the discussions since the passage of the 1970 Clean Air Act has centered on the methods to be used by automotive producers, gasoline refiners, and gasoline additive producers to achieve the exhaust emission standards prescribed by this law for CO, hydrocarbons, and nitrogen oxides. Lead particulate emissions are not regulated. The methods most often discussed are the use of catalytic mufflers to clean up exhaust emissions and the corresponding removal of the lead antiknock additive since it would poison the catalytic surface of these mufflers. Others have advocated the complete redesign of the internal combustion engine, the development of new engines and fuels, and increased use of mass transit systems as solutions to the pollution problem. What is missing from all these discussions, however, is an assessment of these methods from the standpoint of environmental health. Such questions as will the proposed solutions do the job, what will be the consequences for environmental health if these methods fail, and what will be the direct and indirect costs to the general public are important and critical assessments which are lacking at this time, and which will greatly influence the final action on this issue.

This report addresses itself to a discussion of the methods proposed to meet the exhaust emis-

sion standards and an assessment of these methods from the standpoint of technological feasibility of proposed fuel additives and emission control devices, the economics of changes of this magnitude, and the implications for environmental health. The question of whether or not such an assessment can be made free from personal prejudices is real and can be answered by saying that assessments by their very nature are judgments made by individuals with human limitations. This is not in support of the idea that such assessments should not be made, but rather in support of the idea that such assessments should be made and either used as starting points for further discussions by others, or made in conjunction with others as in the Delphi Technique for Technology Forecasting.

The assessment of the implications of the control actions of the Clean Air Act of 1970 is lacking because it is difficult to predict the outcome of such an action due to the complex relationships between economics, public reaction, technology, and Federal intervention. However, the refusal to acknowledge the possibility that what you propose to do to meet a set of regulations may contribute to the problem rather than solve it is not responsible either. This is not to say that human initiative in solving problems should stop; far from it, however, recognition of one's actions and their implications is desperately required by not only the standard setter, but also those directly affected by the regulations of the Clean Air Act and also all segments of the general public.

Technology of Gasoline composition, combustion, and Exhaust Emission Profile

Gasoline Composition

In order to assess the developing technology resulting from the Clean Air Act, it is necessary to start with the state-of-knowledge about the existing technology. In this analysis, the first problem is to characterize the composition of gasoline. In this characterization, it must be remembered that the gasoline refining and blending industry is highly competitive, with the reasoning for selection of various blends and ad-

ditives bound up in science, secrecy, and intuition. The final composition is a function of the chemical composition of the crude oil starting material, the design of process equipment, and the economic value of the different crude fractionates. Other important variables are the climatic conditions of the part of the country in which the gasoline is sold and the types of chemical additives used. Given these many variables, it is not difficult to imagine a large number of different gasoline blends. Even so, gasoline composition and physical properties must have definite ranges, since it must successfully function as a fuel for the internal combustion engine. Remembering this, the problem of characterization of gasoline composition and an understanding of the use of additives is again manageable.

A Task Force Report on Health Intelligence for Fuel and Fuel Additive Registration (3) sponsored by the EPA began to deal with the problems of gasoline characterization and biological test systems for evaluating the health effects of the exhaust emissions. In this exhaust emission characterization, both regulated and nonregulated emissions were considered equally. In this report average compositions for 30 commercial gasolines were given; these data are reproduced in Table 1. A flowsheet describing gasoline manufacture better explains how the different fractions of gasoline are made in a typical refinery. This information is shown in Figure 1, and the gasoline composition is shown in Table 2. In Figure 1, FCCU stands for fluidized bed catalytic cracker unit; CRU means catalytic reformer unit, and Udex is a liquid-liquid extractor unit licensed by Universal Oil Products. A catalytic cracker converts the large hydrocarbon molecules found in crude oil to the smaller hydrocarbon molecules found in gasoline. In operation, a fluidized bed catalytic reactor forces the crude oil up through a bed of catalyst particles. The fluid motion agitates the catalyst particles creating a high degree of turbulence and subsequent high rates of mass transfer which converts the crude oil into the C_6 - C_8 gasoline hydrocarbons. This type of reactor is preferred in this application because of high mass transfer rates and negligible temperature gradients across the reactor. The catalytic reformer (CRU) cracks and

isomerizes straight-run gasolines and light naphthas to increase their octane number. This octane upgrading is due to the production of olefins, formation of low molecular weight compounds, and some isomerization. The Udex process is a liquid extraction with diethylene glycol. This unit is used to separate aromatics such as toluene and benzene from the aliphatic hydrocarbons and is an example of how petroleum refiners can extract many valuable products from crude oil which can be used in gasoline blending and as starting materials for petrochemical industries.

Function of Fuel Additives

A bewildering number of fuel additives is necessary because of the variations in fuels, the variation in engine designs, variations in seasonal temperatures in different regions of the country, and the economics of oil refinery operations. If by the addition of small amounts of chemicals, it is possible to achieve high levels of performance in the automotive engines, then the economic incentive for fuel additives becomes apparent. The use of fuel additives thus allows the oil refiner to divert large quantities of organic chemicals into other markets and thus increase the number of product options open to him. Since most of these organic chemicals are major starting materials for other chemicals industries, the use of fuel additives to free up basic chemicals for other markets is a sound business practice.

The variations in fuel composition and engine designs makes the fuel additive business viable also. For example, engines having lower compression ratios do not need deposit-modifying additives, and changes in olefin content of gasoline requires different antioxidant compounds for these substances to be effective. The introduction of such a variety of compounds can possibly lead to inhibition of function and some antagonism. Therefore, the trend will probably be to develop multifunctional additives with molecular structures capable of performing a variety of similar functions, such as molecules which can function as antioxidants, corrosion inhibitors, and detergents, for example. Tables 3 to 6 provide more information about gasoline composition. Table 3 lists key components in

Table 1. Commercial gasoline properties.

	Premium ^a	Regular ^b	Nonlead
Research octane	99.9-99.4	93.1-91.9	90.3
Motor octane	92.4-91.5	87.0-85.6	82.8
Reed vapor pressure	13.1-13.0	12.9-12.3	10.1
Olefins, %	4.4- 2.6	7.4-10.6	12.6
Aromatics, %	29.7-28.0	21.9-20.3	12.0
Saturates, %	65.9-69.4	70.7-69.1	75.4
Initial boiling point, °F	81-82	84-88	94.0
Final boiling point, °F	410-398	420-390	368
Gravity (API)	60.5-59.9	60.7-63.0	67.5

^a Literature data (3).

^b Range of several factors measured in 30 commercial fuel samples including premiums, regulars, and 91 octane low and nonleaded fuels.

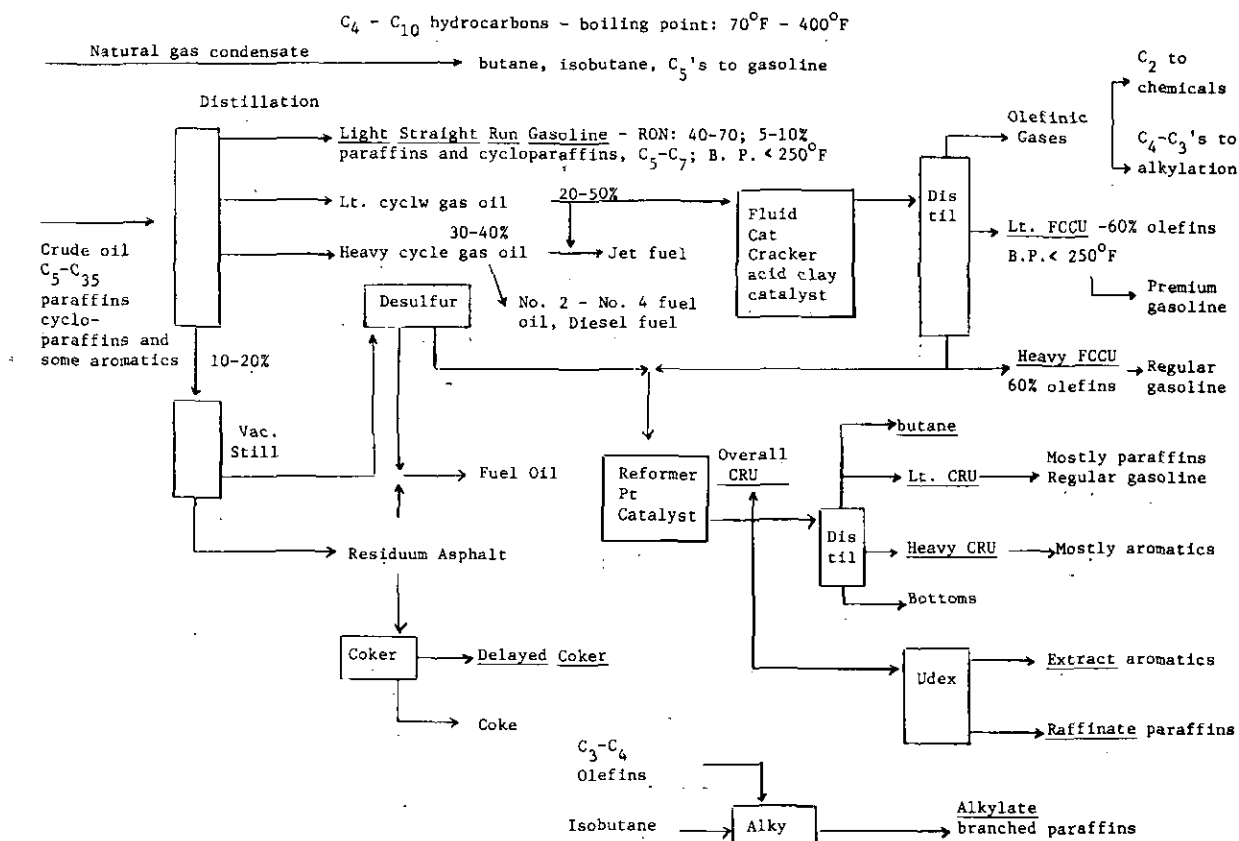


FIGURE 1. Gasoline manufacture.

Table 2. Refinery fractions used in gasoline.^a

Gasoline	Fraction
Premium Typical 98–100 RON ^b	10–20% Butane
	10–30% Light FCCU (olefins)
	40–50% Overall reformat
	10–20% Udex extract
	10–40% Alkylate
	+1000 ppm tetraethyllead
Regular Typical 94–96 RON ^b	10–20% Butane
	20–40% Heavy FCCU
	10–20% Light straight run
	0–10% Udex raffinate
	20–40% Light CRU
	30–50% Overall reformat
	+400 ppm tetraethyllead

^aLiterature data (3).^bResearch octane number

gasoline and concentration ranges for trace metal components. The concentration ranges of these trace elements have become an important component of the feasibility of catalytic mufflers. Tables 4–6 give information on the general classes of additives used in gasoline, their chemical groups, and their consumption statistics. The function of each additive type is given in the next section. The additive consumption statistics reveal that the major production additives for premium and regular gasolines are tetraethyllead (TEL) (72% by weight) and lead scavengers (20% by weight) such as ethylene dichloride and ethylene dibromide.

Function of Fuel Additives

Antiknock Action and Combustion in Spark-Ignited Engines: Knock is defined as preignition of the fuel–air mixture during the compression and ignition strokes of the internal

Table 3. Range of key components in gasoline.^a

Element	Concentration
Lead, g/gal	0.26–3.6
Chlorine, ppm	0.002–0.058
Bromine, ppm	0.001–0.049
Phosphorus, ppm	0.1–22.8
Sulfur, ppm	12–1100
Carbon, wt-%	84.2–86.4
Hydrogen, wt-%	12.7–14.3
Trace elements	
Fe, wt-%	0.5–1.0
Ca, wt-%	0.5–0.9
Mg, wt-%	2–3
Mn, wt-%	0.2–0.3

^a Literature data (3).

combustion engine. In one theory of the mechanism of knock, the compression of a fuel–air mixture to 8–10 atm in fractions of a second results mainly in the oxidation of the saturated paraffinic portion of gasoline (approximately 65–75% by weight) to peroxides, aldehydes, and alcohols, according to Downs et al. (4). If this group of parallel reactions is allowed to continue uninhibited, the oxidation process will reach a rate at which ignition and heat release will occur spontaneously. The explosive potential from peroxides has long been recognized by manufacturers and users of ether, since exposure of ether to air results in the formation of peroxides at an appreciable rate. The resulting detonations of this uncontrolled process, called knock occur before the piston reaches the top of the compression stroke. Since preignition in the compression stroke does not occur at the maximum compression pressure, the knocking condition results in the inefficiency of power derivation and instability in engine operation. Tetraethyllead (TEL) is added to compete for O₂ in the fuel–air mixture during the compression stroke. Since TEL oxidizes to PbO at a rate comparable to the rate of oxidation of fuel paraffins, it can suppress the amount of peroxides, aldehydes, and alcohols formed during the compression stroke. In this way, the concentrations of these paraffin oxidation products

Table 4. Gasoline additives.

Additive	Level, ppm	Comment
Antiknocks		
Tetraethyllead	1000	Best in paraffinic fuels; 10 ⁶ lb/yr
Tetramethyllead		Best in aromatic fuels
Mixtures		
Equilibrated mixtures		Best in certain special blends
Methylcyclopentadienyl- manganese tricarbonyl	100-400	Best in aromatic fuels
Scavengers		
Ethylene dichloride	100	
Ethylene dibromide		
Detergents	>400	Mostly nitrogenous
HTA (Esso)		Hydrogenated tallow amines
F-310 (Chevron)		Primary and secondary amines of 1400 MW polybutene
LZ-580 (Mobile, Amoco)		$\text{C}_{15}\text{H}_{31}-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}$
DMA-4 (Shell)		Amine phosphate
DMA-5A		Amine phosphate (going out)
Corrosion inhibitors		Mainly carboxylic acids
Antioxidants		
Di- <i>sec</i> -butyl- <i>p</i> -phenylenediamine	10-20	
Di- <i>tert</i> -butyl cresol		
Deposit modifiers		
Phenyl dicresyl phosphate		
Metal deactivators		
Disalicylpropanediamine		
Hydrocarbons		
Carrier oils	1000-5000	
Polymers	100-300	

do not reach the levels required for the rapid heat release process of preignition. Therefore, TEL allows the fuel-air mixture to be compressed to the volume at which optimal power is derived from the design of the engine.

In another theory of the mechanism of knock, Polss (5) suggest that uncontrolled combustion in the ignition stroke is a multistage oxidation process and produces hydroperoxides in its first stages. The advancing flame front during combustion produces an increasing pressure and temperature stress which causes hydroperox-

ides to decompose to free radicals. The free radicals initiate chain-branching reactions which cause autoignition of the fuel-air mixture ahead of the flame front. The shock waves from this process strike the cyclinder walls and result in the knocking sound. TEL decomposes to lead oxides which scavenge free radicals from hydroperoxide decomposition. The scavengers for lead antiknock decomposition products are ethylene dichloride and ethylene dibromide. The reaction of these two compounds with lead oxides produces mixed lead halide particulates in the exhaust emissions.

Table 5. Additives used in premium grade automotive gasoline: 1969 consumption.^a

Additive	Price, \$/lb	Use level	1969 consumption, 10 ⁶ lb	10 ⁶ \$
Antiknocks			345.790 ^b	123.440 ^b
Tetraethyllead	0.35	2.34 cc/gal	285.100	101.290
Tetramethyllead	0.36	1.24 cc/gal	60.690	22.150
Methylcyclopentadienyl-manganese tricarbonyl ^c				
Antioxidants			7.242	4.118
2,4-Dimethyl-6- <i>tert</i> -butyl phenol	0.59	7 lb/1000 bbl	1.624	0.958
2,6-Di- <i>tert</i> -butyl-4-methyl phenol	0.57	7 lb/1000 bbl	0.738	0.420
2,6-Di- <i>tert</i> -butyl phenol	0.37	6 lb/1000 bbl	2.953	1.092
<i>N,N'</i> -Bis (1,4-dimethyl pentyl) <i>p</i> -phenylene-diamine	0.87	6 lb/1000 bbl	0.316	0.274
<i>N,n</i> -Butyl- <i>p</i> -aminophenol	0.66	6 lb/1000 bbl	0.189	0.124
<i>N,N'</i> -Diisopropyl- <i>p</i> -phenylenediamine	0.62	7 lb/1000 bbl	0.368	0.228
<i>N,N'</i> -Di- <i>sec</i> -butyl- <i>p</i> -phenylenediamine	0.97	5 lb/1000 bbl	1.054	1.022
Corrosion inhibitors			10.958 ^b	5.102 ^b
Alkyl and amine phosphates	0.51	10 lb/1000 bbl	8.966	4.572
Alkyldiamine naphthalene sulfonate	0.20	50 ppm	0.664	0.132
Fatty acid amines	0.35	50 ppm	0.664	0.232
Fatty acid esters	0.25	50 ppm	0.664	0.166
Deposit modifiers			6.328 ^b	2.301 ^b
Cresyl diphenyl phosphate	0.30	6 lb/1000 bbl	2.531	0.759
Methyl diphenyl phosphate	0.33	6 lb/1000 bbl	1.899	0.626
Methyl phenyl phosphates, mixed	0.35	6 lb/1000 bbl	0.633	0.221
Trimethyl phosphate	0.55	6 lb/1000 bbl	1.265	0.695
Tris(β -chloroisopropyl) thionophosphate ^c				
Detergents			4.904 ^b	1.644 ^b
Fatty acid amides	0.30	50 ppm	3.322	0.996
Surface-active alkyl ammonium dialkyl phosphates	0.41	2 lb/1000 bbl	1.582	0.648
Lead scavengers			96.897 ^b	13.485 ^b
Ethylene dibromide	0.20	0.617 cc/gal	43.315	8.663
Ethylene dichloride	0.09	0.653 cc/gal	53.582	4.822
Calcium sulfonate and dichlorotoluene ^c				
Cresyl diphenyl phosphate ^c				
Metal deactivators				
<i>N,N'</i> -Disalicylidene-1,2-diaminopropane	1.40	1.5 lb/1000 bbl	1.580	2.120
<i>N,N'</i> -Disalicylal ethylenediamine ^c				
Salicylal <i>o</i> -aminophenol ^c				
Rust inhibitors			5.273 ^b	1.060 ^b
Alkylamine salts of orthophosphoric acids	0.47	2 lb/1000 bbl	0.843	0.396
Linoleic acid derivatives	0.15	7 lb/1000 bbl	4.430	0.664
Ammonium dinonylnaphthalene sulfonate ^c				
Fatty acid amides ^c				
Isononyl phenoxy tetraethoxy ethanol ^c				
Isooctyl phenoxy tetraethoxy ethanol ^c				
Total			478.972	153.270

^a Literature data (3).

^b Subtotal.

^c Possible minor use.

Table 6. Additives used in regular grade automotive gasoline: 1969 consumption.

Additive	Price, \$/lb	Use level	1969 consumption, 10 ⁶ lb.	10 ⁶ \$
Antiknocks			263.770 ^b	94.060 ^b
Tetraethyllead	0.35	2.03 cc/gal	227.750	80.900
Tetramethyllead	0.36	0.8 cc/gal	36.028	13.160
Antioxidants			6.686 ^b	3.802 ^b
2,4-Dimethyl-6- <i>tert</i> -butyl phenol	0.59	7 lb/1000 bbl	1.499	0.884
2,6-Di- <i>tert</i> -butyl-4-methyl phenol	0.57	7 lb/1000 bbl	0.681	0.388
2,6-Di- <i>tert</i> -butyl phenol	0.37	8 lb/1000 bbl	2.726	1.008
<i>N,N'</i> -Bis (1,4-dimethyl pentyl) <i>p</i> -phenylene-diamine	0.87	6 lb/1000 bbl	0.292	0.254
<i>N,n</i> -Butyl- <i>p</i> -amino phenol	0.66	6 lb/1000 bbl	0.175	0.115
<i>N,N'</i> -Diisopropyl- <i>p</i> -phenylenediamine	0.62	7 lb/1000 bbl	0.340	0.210
<i>N,N'</i> -Di- <i>sec</i> -butyl- <i>p</i> -phenylenediamine	0.97	5 lb/1000 bbl	0.973	0.943
Corrosion inhibitors			10.115 ^b	4.711 ^b
Alkyl and amine phosphates	0.51	10 lb/1000 bbl	8.276	4.220
Alkyldiamine naphthalene sulfonate	0.20	50 ppm	0.613	0.123
Fatty acid amines	0.35	50 ppm	0.613	0.215
Fatty acid esters	0.25	50 ppm	0.613	0.153
Deposit modifiers			4.867 ^b	1.770 ^b
Cresyl diphenyl phosphate	0.30	5 lb/1000 bbl	1.947	0.584
Methyl diphenyl phosphate	0.33	5 lb/1000 bbl	1.460	0.481
Methyl phenyl phosphates, mixed	0.35	5 lb/1000 bbl	0.487	0.170
Trimethyl phosphate	0.55	5 lb/1000 bbl	0.973	0.535
Tris(β -chloroisopropyl) thionophosphate ^c				
Detergents			2.994 ^b	1.057 ^b
Surface-active alkyl ammonium dialkyl phosphate	0.41	2 lb/1000 bbl	1.460	0.598
Fatty acid amides	0.30	25 ppm	1.534	0.459
Lead scavengers			73.863 ^b	10.289 ^b
Ethylene dibromide	0.20	0.51 cc/gal	33.114	6.622
Ethylene dichloride	0.09	0.538 cc/gal	40.749	3.667
Calcium sulfonate and dichlorotoluene ^c				
Cresyl diphenyl phosphate ^c				
Metal deactivator				
<i>N,N'</i> -Disalicylidene-1,2-diaminopropane	1.40	2 lb/1000 bbl	1.946	2.724
<i>N,N'</i> -Disalicylal ethylenediamine ^c				
Salicylalo-aminophenol ^c				
Rust inhibitors				
Alkyl amine salts of orthophosphoric acids	0.47	2 lb/1000 bbl	0.779	0.366
Linoleic acid derivative	0.15	7 lb/1000 bbl	4.089	0.613
Ammonium dinonyl naphthalene sulfonate ^c				
Fatty acid amides ^c				
Isononyl phenoxy tetraethoxy ethanol ^c				
Isooctyl phenoxy tetraethoxy ethanol ^c				
Total			369.109	119.392

^aLiterature data (3).^bSubtotal.^cPossible minor use.

Detergents: Carburetor detergents are polar molecules which adhere to the metal surfaces of the carburetor. This coating action prevents deposition of materials which could build up on these surfaces and thus change the dimensions of the carburetor flow passages and ultimately plug the carburetor. Detergents are nitrogen-based compounds such as amines, amides, amine neutralized alkylphosphates, imidazolines and succinimides. The molecules' polarity is a result of the nitrogen atoms. The surfactant qualities necessary for spreading onto surfaces comes from the nature of the other components of the carburetor detergent molecule.

Corrosion Inhibitors. Gasoline is transported from the refinery to the distributors through long pipelines and storage tanks which are subject to rust. Rust particles can plug fuel filters if uncontrolled. Corrosion inhibitors which are fuel additives are high molecular weight substances with at least one strong polar group such as a carboxylic or phosphoric acid or their neutralized derivatives. The polar group binds to the metal surface and decreases the possibility of water coming in contact with the metal. This eliminates the electrolyte necessary to effect the electrochemical processes involved in corrosion. Diimides have also been shown to be effective corrosion inhibitors for fuels. Again, the molecular requirements for effective corrosion inhibitors are a polar group which binds to the metal surfaces and coats them, and nonpolar group which juts out into the fuel.

Antioxidants: The ability of the olefinic portions of gasoline to oxidize and polymerize to form a decomposition product referred to as gum, obligates the need for antioxidant fuel additives. Phenylenediamines such as di-*sec*-butyl *p*-phenylenediamine and hindered phenols such as di-*tert*-butyl cresol are common antioxidants for gasoline. These compounds are also antioxidants for plastic and rubber products. Antioxidants also scavenge peroxides formed during storage of gasoline and thus assist as antiknock compounds. The scavenging ability of these compounds originates from their function of interrupting or terminating the oxidation and polymerization reactions of the olefinic portion

of the gasoline. Generally the hindered phenols are more effective antioxidants in lower olefin content gasolines, and the phenylenediamines are more effective antioxidants for higher olefin content gasolines. However, phenylenediamines catalyze the oxidation of mercaptans to disulfides, the so-called fuel sweetening process.

Deposit Modifiers: High compression ratios of 10:1 cause decomposed TEL and other residues on cylinder walls to glow due to the high temperatures of the compression stroke. This glowing phenomenon can cause surface ignition to occur before normal spark ignition and thus result in knock. Deposit modifiers such as cresyl diphenyl phosphate and methyl diphenyl phosphate react with PbO and form lead phosphates which have higher glow temperatures. In effect, the volume of cylinder deposits is not reduced, but the thermal and electrical properties of these deposits are modified to reduce the frequency of surface ignition. Lower compression engines do not require these additives since the cylinder wall temperatures do not reach the glow temperature of lead oxides.

Metal Deactivators: Because trace metals in gasolines have the ability to catalyze decomposition of peroxides to free radicals and thus promote decomposition of olefins, fuel additives called metal deactivators are necessary to chelate the metals and cause their deactivation as catalysts. The most widely used compound for this function is *N,N'*-disalicylidene-1,2 propanediamine. An important question with this particular additive is the nature of the exhaust products of the chelated metal ions. Because of the 2000–2900°F temperatures achieved during combustion, these chelated metals most probably are converted to oxides. What effect these substances will have on the catalytic converter, and how they will react with other exhaust constituents, and what the final exhaust products are, are unknown at this time.

Exhaust Emission Profiles

Federal regulations and changing engine designs have changed the exhaust emission profile substantially within the last six years.

Minor engine modifications such as lower compression, leaner mixtures, spark retardation at idle, and limited use of air pumps have lowered hydrocarbon and carbon monoxide exhaust concentrations of these atmospheric pollutants to about 25% of what they were before the use of these devices. These facts are demonstrated by Voelz et al. (6) and are shown in Table 7.

Table 7. Average exhaust gas emissions for U.S. vehicles by age group.

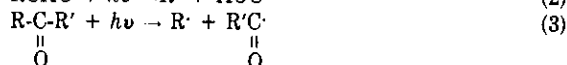
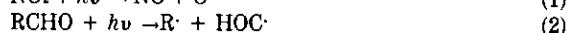
City and year group	Average exhaust emissions			
	2500 rpm		Idle	
	HC, ppm	CO, %	HC, ppm	CO, %
Los Angeles				
Pre-66	390	3.1	720	4.9
66-67	220	1.3	370	3.1
68-69	190	1.2	350	3.7
70	130	0.9	230	2.4
Chicago				
Pre-66	410	2.9	690	4.4
66-67	330	2.4	590	4.4
68-69	220	1.2	350	3.5
70	120	0.9	250	2.6

^aThese data are vehicles tested at the condition specified in the cities shown. Data of Voelz et al. (6).

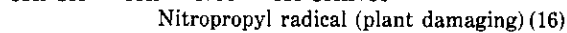
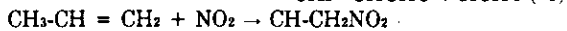
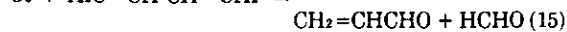
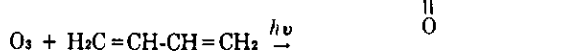
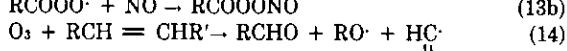
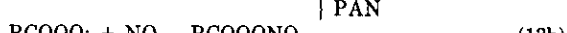
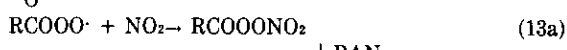
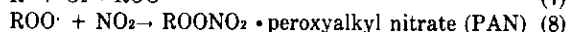
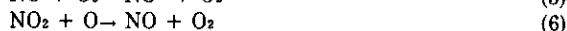
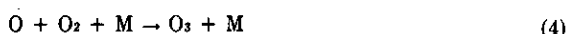
These modifications, however, have had little effect on reducing nitrogen oxide emissions. It is the nitrogen oxides which are involved with the formation of nitrogen dioxide (NO₂). This compound then reacts with peroxyacyl free radicals to form the eye irritant and plant damaging material called peroxyacyl nitrate (PAN).

There are two primary photochemical reactions occurring in the lower atmosphere. Nitrogen dioxide decomposes photochemically to form nitric oxide and nascent oxygen. The other primary photochemical reactions occurring in the lower atmosphere are the degradation of aldehydes and ketones to form free radicals. Once these two major reactions are initiated, a large number of secondary reactions can occur which produce the major components of smog, eye irritants, and plant damaging materials. A summary of these important reactions (7) are given in eqs. (1)-(20).

Primary Photochemical Reactions:



Secondary Chemical Reactions:



The types of hydrocarbons, oxygenated hydrocarbons, and polynuclear or polycyclic hydrocarbon particulates and their concentration ranges in the exhaust from simple hydrocarbon fuels are shown in Tables 8-11. It is not possible to determine the fractions of these substances contributed by the combustion of fuel additives since the product distribution of such a large number of simultaneous parallel and series reactions is unknown. Tables 8 and 9 have been given by the EPA (3). In Table 8, it is interesting to note that hydrocarbon (HC) and carbon monoxide emissions for a hot start engine are about one-half of the concentrations for a cold start. Nitrogen oxides concentrations are essentially unaffected by whether or not the engine is warm or cold.

The analysis of exhaust emissions for polycyclic hydrocarbon particulates for European road tests with a VW 1300 is given in Table 10. The chemical structures of these polynuclear aromatics are given in Table 11.

Table 8. Emission profiles; current systems, '71 Ford, LA-4 cycle.

	Emissions, g/mile	
	Cold start	Hot start
HC	2.32 ± 0.065	1.81 ± 0.078
CO	39.30 ± 1.910	15.60 ± 2.230
NO _x	4.02 ± 0.41	4.06 ± 0.13
Paraffin	1.13 ± 0.049	0.90 ± 0.05
Olefin	1.07 ± 0.058	0.84 ± 0.036
Aromatic	0.15 ±	0.10 ± 0.009
Dilution Ratio	10.11 ± 0.15	11.23 ± 0.14
Exhaust Vol CF/Mile	92.87 ± 1.65	82.27 ± 0.47
Methane	0.169 ± 0.005	0.091 ± 0.010
Ethane	0.031 ± 0.001	0.021 ± 0.005
Acetylene	0.208 ± 0.004	0.158 ± 0.011
Paraffins		
Isobutane	0.004	0.005
<i>n</i> -Butane	0.045 ± 0.006	0.077 ± 0.016
Isopentane	0.051 ± 0.005	0.085 ± 0.013
<i>n</i> -Pentane	0.008	0.019 ± 0.001
Hexanes	0.111 ± 0.017	0.108 ± 0.002
Heptanes	0.120	0.118
Total	0.342 ± 0.087	0.432 ± 0.083
Olefins		
Ethylene	0.272 ± 0.006	0.212 ± 0.002
Propylene	0.139 ± 0.005	0.117 ± 0.006
Butenes	0.077 ± 0.002	0.026 ±
2-Methyl-1-butene	0.012 ± 0.001	0.011 ± 0.002
3-Methyl-1-butene	0.007 ± 0.001	0.003
Others	0.164 ± 0.009	0.146 ± 0.039
Total	0.670 ± 0.022	0.572 ± 0.050
Aromatics		
Benzene	0.188 ± 0.008	0.142 ± 0.024
Toluene	0.201 ± 0.007	0.142 ± 0.020
Ethylbenzene	0.046 ± 0.001	0.031 ± 0.001
<i>o</i> , <i>p</i> -Xylene	0.078 ± 0.005	0.050 ± 0.002
<i>m</i> -Xylene	0.070 ± 0.004	0.047 ± 0.003
Mesitylene	0.011 ± 0.001	0.005 ±
1,2,4-Trimethylbenzene	0.054 ± 0.004	0.035 ± 0.002
Others	0.061 ± 0.003	0.040 ± 0.002
Total	0.724 ± 0.023	0.504 ± 0.045

The profile is given by Grimmer et al. (8) and shows the main components, their average amounts in exhaust, their weight per cent in the exhaust, and their carcinogenic activity (Table 10). Carcinogenic activity is defined as follows: a negative sign (-), inactive; plus sign (+) mild carcinogen; three plus signs (+++), a strong carcinogen. It is worthy of note, that 5.04 wt-%

of exhaust polycyclic aromatic hydrocarbon particulates are carcinogens, and that the bulk of the particulates (87.14 wt-%) is composed of phenanthrene, anthracene, pyrene, and fluoranthene. This type of distribution which favors the lower molecular weight polycyclic hydrocarbons is quite possibly a function of the residence time of combusted gasoline in the cylinder head and

Table 9. Oxygenates in exhaust from simple hydrocarbon fuels.

Oxygenate	Concentration range, ppm ^a
Acetaldehyde	0.8- 4.9
Propionaldehyde (+ acetone) ^b	2.3-14.0
Acrolein	0.2- 5.3
Crotonaldehyde (+ toluene) ^c	0.1- 7.0
Tigraldehyde $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$	<0.1- 0.7
Benzaldehyde	<0.1-13.5
Tolualdehyde	<0.1- 2.6
Ethylbenzaldehyde	<0.1- 0.2
<i>o</i> -Hydroxybenzaldehyde (+ C ₁₀ aromatic) ^d	<0.1- 3.5
Acetone (+ propionaldehyde) ^b	2.3-14.0
Methyl ethyl ketone	<0.1- 1.0
Methyl vinyl ketone (+ benzene) ^e	0.1-42.6
Methyl propyl (or isopropyl) ketone	<0.1- 0.8
3-Methyl-3-buten-2-one	<0.1- 0.8
4-Methyl-3-penten-2-one	<0.1- 1.5
Acetophenone	<0.1- 0.4
Methanol	0.1- 0.6
Ethanol	<0.1- 0.6
C ₈ alcohol (+ C ₈ aromatic) ^f	<0.1- 1.1
2-Buten-1-ol (+ C ₈ H ₈ O)	<0.1- 3.6
Benzyl alcohol	<0.1- 0.6
Phenol + cresol(s)	<0.1- 6.7
2,2,4,4-Tetramethyltetrahydrofuran	<0.1- 6.4
Benzofuran	<0.1- 2.8
Methyl phenyl ether	<0.1
Methyl formate	<0.1- 0.7
Nitromethane	<0.1- 5.0
C ₄ H ₈ O	<0.1
C ₅ H ₈ O	<0.1- 0.2
C ₅ H ₁₀ O	<0.1- 0.3

^aValues represent concentration levels in exhaust from all test fuels.

^bData represent unresolved mixture of propionaldehyde + acetone. Chromatographic peak shape suggests acetone to be the predominant component.

^cToluene is the predominant component.

^dThe C₁₀ aromatic hydrocarbon is the predominant component.

^eBenzene is the predominant component.

^fThe aromatic hydrocarbon is the predominant component.

the exhaust manifold, and the rate constants associated with the formation of this group of polycyclic compounds (9).

Gross (10) has examined the influence of fuel and vehicle variables on the formation of polycyclic hydrocarbons in the exhaust gases. This comprehensive study measures benzo(a)pyrene (BaP) and benz(a)anthracene (BaA) as a function of fuel composition, engine deposits, and engine designs which includes studies with uncontrolled emission engines, modified engines, engines with thermal converters on the

exhaust, and engines with monel-platinum catalytic converters on the exhaust. The results of this study are particularly good in clarifying the quantitative changes in the amounts of benzo(a)pyrene and benz(a)anthracene which are produced during automotive operation as a function of these many variables. Therefore, these results will be presented in detail. Table 12 gives the key for each engine-exhaust system design; Table 13 defines the fuel and the resulting engine deposits; Tables 14 and 15 show how these variables affect the amounts of BaP

and BaA in the exhaust. Figure 2 compares the emission output for each engine design with a fuel containing 46 wt-% aromatics.

Tables 14 and 15 show for the uncontrolled exhaust system of the 1966 Plymouth (P) that amounts of dibenzo(a)pyrene and

Table 10. Polycyclic hydrocarbon profile in exhaust emissions from European road tests with VW 1300^a.

Compound	Emissions		Carcinogenic activity
	Total, μg	Weight per cent	
Phenanthrene	2595.0	40.74	-
Anthracene	964.0	15.15	-
Pyrene	1168.4	18.33	-
Fluoranthene	822.1	12.92	-
Benzo-(a)anthracene	102.6	1.63	+
Chrysene	67.8	1.07	+
Benzo(e)pyrene	54.1	0.86	-
Benzo(a)pyrene	83.8	1.32	+++
Anthanthrene	42.7	0.68	-
Benzo(ghi)perylene	253.2	3.98	-
Dibenz(a,h)-anthracene	64.9	1.02	+++
Coronene	146.1	2.30	-

^aData of Grimmer et al. (8).

Table 11. Structure of polycyclic hydrocarbons.

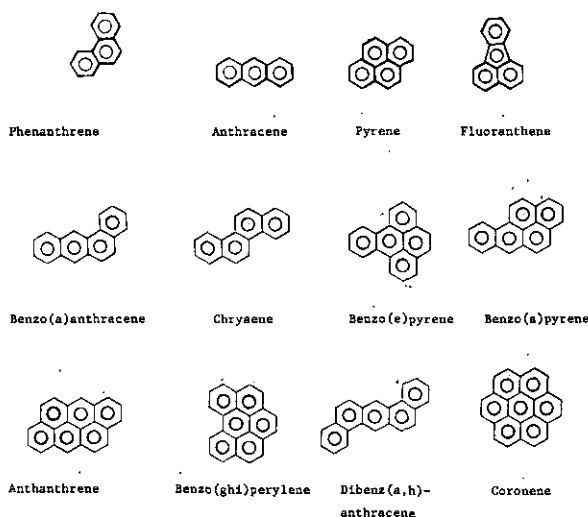


Table 12. Emission test vehicles.

Code	Model, year	Emission-control system
P	1966 Plymouth, 318, V-8	No emission control (NC)
Q	1968 Chevrolet, 307, V-8	Engine-modification (EM)
R	1970 Chevrolet, 350, V-8	EM with spark retard (TCS System)
Q-RAM	1968 Chevrolet, 307, V-8	Experimental air-injected RAM thermal reactor
R-CAT	1970 Chevrolet, 350, V-8	Experimental monel catalyst + platinum catalyst (Engelhard PTX-5)

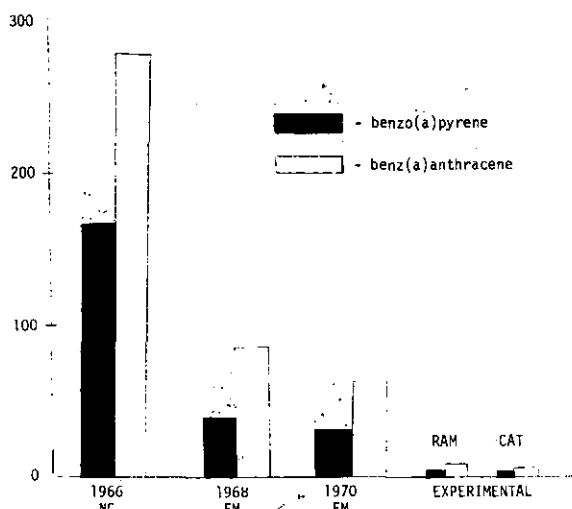


FIGURE 2. Hydrocarbon emissions with various engines. Test fuel, 46% aromatic, 3 ppm BaP; 3 g Pb/gal except in CAT design, in which 0 g Pb/gal used.

benz(a)anthracene increased as the weight per cent of aromatics in the fuel increased. Table 15 shows that for the uncontrolled exhaust system (P), the nature of the deposits on the cylinder wall influences the quantity of BaP and BaA produced. Apparently, leaded gasoline deposits give more of these compounds than do the deposits from unleaded gasoline. Table 14 shows also that for car P, the BaP content of the exhaust is essentially not a function of lead content of the fuel, whereas the BaA content increases slightly with lead content of the fuel. The two modified engines (EM), cars Q and R essentially reduce BaP and BaA emissions by

Table 13. Fuel composition-Engine Deposit Relationship.

Code Deposit		Fuel - deposit
A	A	Commercial lead-free premium used from the beginning of tests
A.5	A	Commercial lead-free premium, + 0.5 g Pb/gal
B3P	B	Commercial leaded (2-3 g TEL/gal) premium with phosphorus additive

one fourth of the quantities shown for car P for all variations in fuel composition. Figure 2 shows how all five engine designs compare on BaP and BaA emissions for test fuels containing 46% aromatics and 3 ppm BaP. Engines P, Q, R, and Q-RAM were tested with fuel containing 3 g TEL/gal, and R-CAT with 0 g TEL/gal since the Pb would poison the catalytic surface of the converter.

If it is assumed that a higher percentage of aromatics is used as an alternative for leaded verters, it is possible to estimate the potential levels of benzo(a)pyrene and benz(a)anthracene released in the air. If gasoline consumption is assumed to be approximately 10^{11} gal/yr and twice the present amounts of BaP and BaA approximates the total concentration of carcinogenic material produced in exhaust emissions, then the concentration range of carcinogenic material in the atmosphere could range from 1000 lb/yr for the catalytic exhaust system to about 200,000 lb/yr for the uncontrolled exhaust system. Since these compounds are resistant to degradation by environmental processes, they will persist, their concentration will increase, and they will be widely distributed.

Catalytic Converters and Thermal Converter Emission Control Devices

Reduction-oxidation catalytic converters and the thermal noncatalytic converter-lead trap system have been offered as solutions to the exhaust emission control problem. The operating principles of both designs are to reduce nitrogen oxides to N_2 and O_2 , and to oxidize CO to CO_2 and hydrocarbons and polycyclic aromatics to CO_2 and H_2O . The noncatalytic converter-lead trap

design offers the additional feature of lead particulate trapping and can be used with presently available fuels. Leaded gasoline cannot be used with the catalytic mufflers. Of the two designs, it appears that the catalytic converter will be adopted as an interim solution to meet the 1976 exhaust emission standards. For this reason, the thermal noncatalytic-lead trap system will not be discussed. The design does have merit and in lieu of the present gasoline shortages, more attention to the exhaust emission characterization from the device should be considered since exhaust lead particulates would be reduced by 80% (11, 12) and the use of TEL in gasoline would free up valuable aromatic feedstocks.

The design of this catalytic system has a reducing catalytic muffler on each exhaust manifold pipe followed by one oxidation catalytic muffler on the exhaust pipe preceding the muffler. The feasibility of constructing such a multipurpose catalytic converter to operate effectively for extended periods of time and under such a wide variety of operating conditions to which it will be subjected is questionable. Besides the obvious factors which will cause the catalyst to break apart such as thermal shock from a hot exhaust on a cold catalyst at engine startup, and mechanical breakup caused by operation, other sources which can shorten catalyst life are the trace metals (10-20 ppm range) which end up in gasoline as fractionation residues. It is understood that lead must be removed from gasoline for these devices to achieve their 50,000 mile life expectancy. With leaded gasoline, the catalytic surface becomes poisoned after approximately 12,000 miles and then the situation is one of the uncontrolled exhaust. Other questions associated with this device are increases in engine operating temperatures caused by increased back pressure of exhaust gas passage through the catalytic muffler with associated problems of lubricant degradation and engine malfunction. Such a situation would result from using richer mixtures which would produce better gas mileage, but may conceivably shorten engine life substantially.

Presently, it appears that a Pt/Pd catalyst will be used in these mufflers. At one time almost all of the transition metals were tried in this application since it had been shown that

Table 14. BaP and BaA emissions as a function of engine design, aromatic content of fuel, and tel lead content of fuel.

Aromatics Vehicle in fuel, wt-%		Emissions, $\mu\text{g/gal.}$					
		BaP			BaA		
		0 Pb	0.5 g Pb/gal	3.0 g Pb/gal	0 Pb	0.5 g Pb/gal	3.0 g Pb/gal
P	11	56	—	56	126	—	155
	28	78	63	59	130	86	157
	28	36	18	29	49	30	46
	46	125	—	127	196	—	258
Q	28	11	8.9	36	28	20	75
	28	14	3.5	3.4	15	13	15
	46	30	—	32	55	—	63
R	28	48	36	26	70	61	51
	46	26	—	17	60	—	52

Table 15. Effect of deposit fuel composition on polycyclic hydrocarbon emissions.

Test Vehicle	Aromatics, wt-%	BaP, $\mu\text{g/gal}$		BaA $\mu\text{g/gal}$	
		Deposit		Deposit	
		A	B	A	B
P	46	57	125	94	196
	28	39	78	51	130
	46	54	127	124	258
	28	36	78	49	130
	28	18	63	30	86
	28	29	59	46	157
Q	46	12	30	23	55
	28	15	11	17	28
	28	14	11	15	28
	28	3.5	8.9	13	20
	28	3.4	36	15	75

NO was readily adsorbed onto these materials, a necessary step in the catalytic decomposition of NO to N_2 and O_2 . Thermodynamically, the equilibrium constant for the decomposition of NO is more favorable at lower temperatures ($K_{\text{NO}} = 3.236 \times 10^2$ at 1500°K ; $K_{\text{NO}} = 1.208 \times 10^4$ at 1000°K ; and $K_{\text{NO}} = 1.413 \times 10^{11}$ at 400°K). The reduction of NO produces O_2 which is then used to oxidize CO and hydrocarbons, but the thermodynamics would favor the reduction catalyst after the oxidation catalyst due to the lower temperatures and subsequent faster reaction rate of NO decomposition. The proponents of the

thermal noncatalytic converter argue that the catalytic converters are impractical and expensive. The two main supporters of the thermal converters which could be used with either leaded or unleaded gasoline are du Pont and Ethyl Corporation. Ethyl Corporation is the main producer of TEL in the United States. The operating principle of the thermal converter is to convert unburned hydrocarbons and CO to CO_2 and H_2O , decompose NO to N_2 and O_2 and trap lead particulates. The operating temperatures range from 1200°K (du Pont design, $K_{\text{NO}} = 2 \times 10^3$) to 1500°K (Ethyl design, $K_{\text{NO}} = 3.24 \times 10^2$).

It is the author's opinion that the catalytic emission control device is an example of a solution for a problem after the fact. The main questions of how the design of the internal combustion engine and the composition of the fuel can be changed to reduce levels of exhaust emissions which contribute to smog formation and associated health problems, are unaddressed. It is realized, however, that such solutions require time to invent and implement, and require substantial monetary research commitments. Even so, the catalytic emission control device is being sold as the method to meet the standards of the Clean Air Act of 1970, even though it may be of questionable functioning ability. The muffler has been shown by Campion (13) to catalyze the oxidation of sulfur occurring in gasoline as a residue, to SO_3 so that higher concentrations of SO_3 are produced by use of catalytic mufflers than without catalytic mufflers. In the atmosphere SO_3 is hydrolyzed to sulfuric acid mist which can be adsorbed onto particulates or fallout as acid rainfall.

The design of the catalytic muffler undoubtedly will be improved to the point that the Clean Air Act Standards or regulated exhaust emission levels for hydrocarbons, CO, and nitrogen oxides will be met. It is the nature and quantity of the unregulated emissions which cause the most concern. The number of books and journal articles dealing with the catalytic nature of platinum are extensive, because its chemical characteristics facilitate such a wide variety of gas-phase reactions. The ability of the platinum catalyst to oxidize sulfur to SO_3 raises the real questions of what other reactions are possible on this surface at exhaust gas temperatures and pressures. Then, what is the breakup rate of these catalysts with the associated questions concerning the discharge of unregulated emissions into the environment of platinum metal, platinum compounds and complexes, and the refractory catalyst support matrix? If indeed the catalyst is breaking up at a significant rate, how much of the catalyst can be lost out the exhaust pipe before the catalyst becomes ineffective in reducing the regulated emissions to the prescribed levels? In other words, how much catalyst can be lost before the situation of the uncontrolled exhaust is reached?

Economics of a Ban on Leaded Gasoline

The economic impacts of the removal of lead from gasoline are significant and complex. These effects are significant because the total sales of the major supplier of TEL would be cut in half and because the use of TEL frees up a large quantity of aromatic feedstocks which are diverted into the petrochemical industry. The ban on lead in gasoline will not only affect several obvious interest groups, e.g., automobile manufacturers, oil refiners, lead additive producers, and lead producers, but also other chemical processors in a less well known manner.

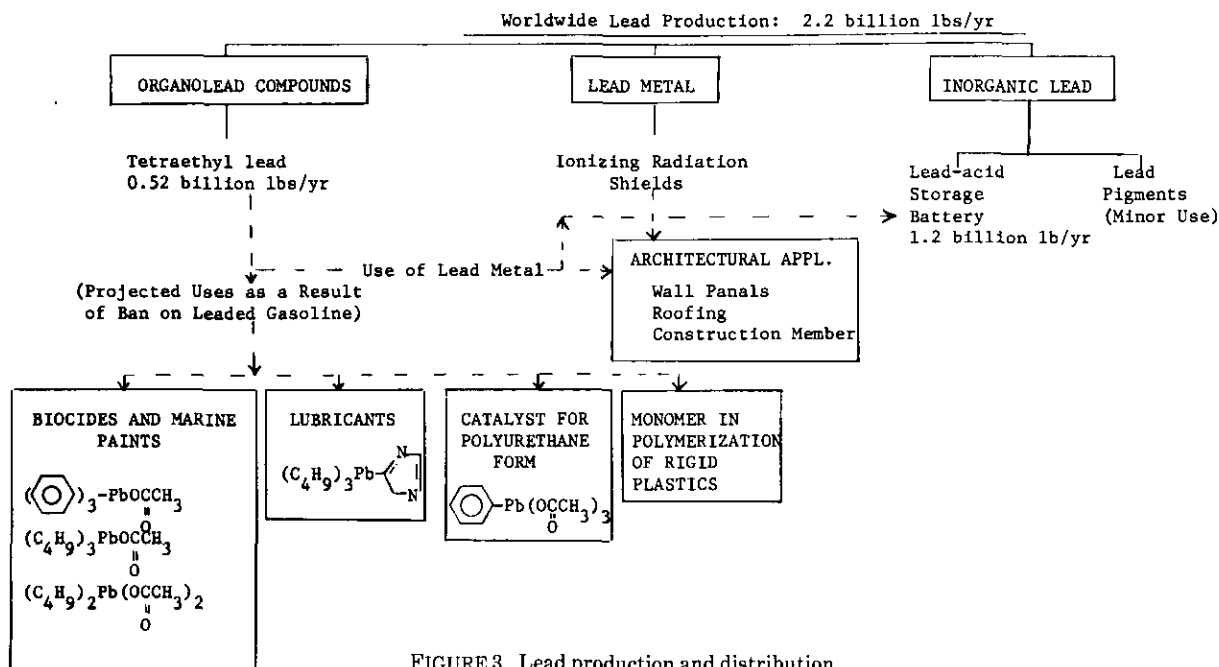
One very probable alternative to leaded gasoline if it is available, is the use of a higher percentage by weight of aromatics. Chohey (14) has noted some of the economic implications of such a switch to higher percentages of aromatics in gasoline. The operations of the oil refiners, additive makers, automobile manufacturers, and lead producers are highly connected. Since all four deal with large volume products, large amounts of capital and equipment are committed by each industry. A change in the products of one industry, therefore, has a very profound effect on the products of the other three industries. In connection with these facts, it must be remembered that once a particular plant design has been decided on by industry, a timetable has been fixed which shows how much time is required for plant construction, and how long the plant must operate at its rated capacity to pay for the investment and to realize a profit. Part of this profit is applied to the construction of new plant facilities to perpetuate the operations of the industry. The point here is that a significant lead time is required to implement a product change and that a change cannot be affected immediately.

In leaded gasoline, the primary aromatics used, benzene, toluene, and the xylenes, already amount to approximately 20–30% by weight. In unleaded gasolines, the weight percentage of these aromatics could be as high as 46% in premium fuels. Even for engines designed to run on 91–92 Research Octane Number (RON) gasolines, the weight percentage of aromatics must be increased 5–10% above regular gaso-

line compositions if this is the method chosen to replace the octane boosting antiknock properties of TEL. For the sake of illustration, assuming that all gasolines will contain about 46% aromatics by weight, such a tremendous increase in demand by gasoline manufacturers for these basic chemical feedstocks would have economic impacts on several obvious markets and several unexpected markets. Current consumption of gasoline according to EPA figures amounts to approximately 10^{11} gal/yr. An increase of 10–20% by weight of aromatics in gasoline would produce a demand for 10–20 billion gal/yr more of these chemicals. Several changes would be in the product distribution of oil refineries because the major portion of these aromatic chemicals are produced from the distillate streams of crude oil refining. Already a major portion of these aromatic feedstocks are being diverted into low-sulfur fuels for power generation plants due to the SO_2 regulations of the Clean Air Act. It is the increased demand for aromatics which would produce unexpected economic results. For example, xylenes are major starting petrochemicals for phthalic anhydride and terephthalic acid which are used respectively to make PAE plasticizers and

polyester fibers (Dacron, Kodel, and Fortrel). Therefore, the increased demand for xylene would eventually surface as an increase in the price of flexible PVC plastics and polyester textile products. Benzene is widely used in the production of styrene monomer for making polystyrene products, and for making phenols. Toluene is a valuable solvent and starting material for the making of intermediates such as nitrotoluene and toluenediamine. The point here is that there is a complex relationship between economics, plant operations, products, legislation, and health, and that an action in one of these areas does not occur independently as an isolated event.

The lead industry has been searching for alternative uses for the lead metal which would be available for other uses if it is legally banned for the production of the octane boosting antiknock TEL (15). Research sponsored by the International Lead Zinc Research Organization, Inc. (ILZRO) is underway to divert this lead into new organolead compounds, new or increased uses of inorganic lead compounds, and new applications of lead metal. The flowsheet in Figure 3 shows the present uses of lead in-



dictated by solid lines, and projected uses for lead indicated by the broken lines.

Organolead derivatives have been tested for their use as biocides, lubricant additives, urethane polymerization catalysts and monomers for polymerization. Inorganic lead derivatives continue to be used in paint pigments and lead acid storage batteries. Since lead use in the storage battery accounts for about half the production of lead, research is underway to use oxygen from the air as the cathode reactant. This design change would improve the operating range of the battery so that it could compete more favorably with newer, more expensive, higher-energy density batteries. New markets for lead pigments would be in paints for corrosion resistance for steel. Expanded use of lead metal in architectural applications has also been studied, particularly the increased use of lead roofing shingles, wall panels, and exterior building members.

Health Effects of the Alternatives for TEL Substitutes for TEL

The use of higher percentages of aromatics in the gasoline to achieve the same octane boosting, antiknock properties that TEL supplies and the associated health problems with the use of this alternative to TEL have been discussed previously. The incentive to develop substitutes for TEL is high because of the market potential of the product. Metal carbonyl compounds such as iron pentacarbonyl and manganese carbonyl, and aromatic amines such as ethylaniline have been proposed as substitutes for TEL (16). Iron pentacarbonyl has been rejected because its combustion product, ferric oxide resulted in extensive engine wear. Manganese carbonyl was too expensive. Ethylaniline was rejected because it was 55 times less efficient than TEL at providing antiknock characteristics to gasoline.

Efficacy of Manganese Antiknock Substitute for TEL

A particular manganese antiknock additive, methylcyclopentadienylmanganese tricarbonyl (MCMT) $[\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3]$, has been singled out for detailed consideration because the major producer of TEL, Ethyl Corporation, has shown

that this additive at a concentration of 0.25 g Mn/gal has the same octane boosting and antiknock characteristics as TEL (17). In current leaded gasoline blends, TEL is present in the amount of 1.5 to 2.0 g/gal. Using U.S. Tariff Commission unit price information for organic chemicals produced in 1970, TEL sold for \$0.58/lb. At the present gasoline use level of TEL, this cost adds about 0.2¢ to the price of a gallon of gasoline. It is estimated that MCMT used at the rate of 0.25 g Mn/gal would add between 2.5 and 4¢ to the price of a gallon of gasoline. Since the unleaded gasolines which use a higher percentage of aromatics to obtain higher octane ratings cost 2–4¢/gal more than leaded gasolines, the use of MCMT would be economically competitive with the higher percentage aromatic no-lead gasolines. The efficacy of MCMT was further substantiated by a report from HEW (18) in 1962 which cited this particular additive as being twice as effective in raising the octane number as TEL.

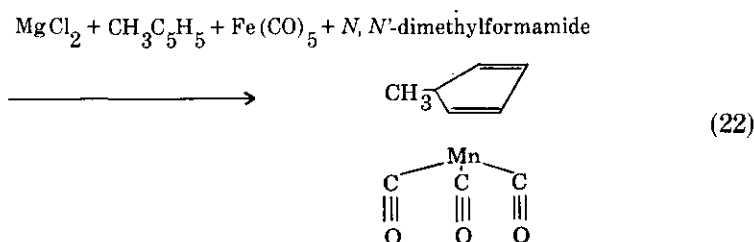
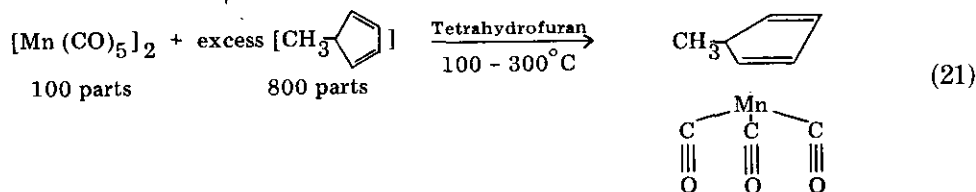
MCMT is not a new compound. It is currently being produced at the level of a 10^6 lb/yr. In 1959, Ethyl Corporation announced higher octanes could be obtained with this manganese additive in combination with TEL (19). MCMT has a synergistic effect with TEL on improving antiknock properties of gasoline. The additive promotes and extends the effect of TEL in raising octane number and preventing engine knock. Although the mechanism of action of antiknock compounds is not completely known, it has been postulated by Girelli and Orlandi (20) that the manganese additive in the presence of TEL decomposes to MnO at a faster rate than TEL decomposes to PbO. It is the presence of MnO which precedes the formation of PbO that breaks the chain of reactions of gasoline combustion which in the presence of TEL alone would continue unabated until knocking occurred before the appearance of PbO.

Preparation of Methylcyclopentadienylmanganese Tricarbonyl and Combustion Products in the Exhaust

MCMT is one of the so-called "sandwich" compounds and is structurally similar to ferrocene, in that the methylcyclopentadiene ligand is π -

bonded to manganese. The methylcyclopentadienylmanganese tricarbonyl is further classified as a penetration complex because dis-

similar ligands are bonded to the manganese atom. MCMT has been synthesized by several methods. [eqs. (21) and (22)].



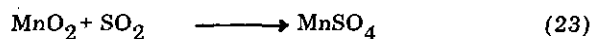
Reaction (22) is run with the use of a Mn electrode, pressured to 1000 psi with CO_2 ; 25–30V and current density of 0.1 A/cm² at 195°C for 3 hr.

Scavengers, such as ethylene dichloride and ethylene dibromide, in the gasoline probably would not be used with this Mn additive so that there could be some MnO , or other oxides of manganese such as MnO_2 , Mn_2O_3 and Mn_2O_4 in the exhaust emissions of uncontrolled vehicles. These compounds would be particulate in nature. Other possible gaseous exhaust emissions would be carbon monoxide (CO), methylcyclopentadienone ($\text{CH}_3\text{C}_5\text{H}_3\text{O}$), and cyclopentadienecarboxaldehyde ($\text{C}_5\text{H}_4\text{CHO}$). There is also a possibility that methylcyclopentadiene could participate in the formation of polycyclic aromatic exhaust particulates.

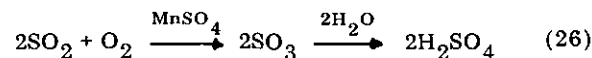
Atmospheric Reactions of Exhaust Products from Mn Additive

Methylcyclopentadienylmanganese tricarbonyl has been used as an additive to fuel oil to suppress the formation of SO_2 and NO_2 in the flue gases (16). Manganese dioxide, MnO_2 , form-

ed during combustion, readily reacts with SO_2 and NO_2 to form soluble sulfates, dithionates, and nitrates, (21) by the reactions (23)–(25):



Manganese sulfate, however, will catalyze the formation of sulfur trioxide from sulfur dioxide. Sulfur trioxide then reacts with water vapor to form sulfuric acid [eq. (26)].



This reaction proceeds very rapidly in foggy atmospheric conditions. It has been shown (21) that in a fog, on assuming a water vapor content of 200,000 $\mu\text{g}/\text{m}^3$, a Mn concentration of 0.2 $\mu\text{g}/\text{m}^3$ and a SO_2 concentration of 1,750 $\mu\text{g}/\text{m}^3$

produces about $25 \mu\text{g}/\text{m}^3$ of H_2SO_4 per hour. The rate of formation of H_2SO_4 triples when the Mn concentration doubles, and increases linearly with an increase in SO_2 concentration. It is also significant that whereas other materials such as platinum, graphite, charcoal, vanadium pentoxide, chromic oxide, ferric oxide, and nitrogen dioxide will catalyze the oxidation of SO_2 to SO_3 , MnSO_4 is the most active. EPA air quality data for 1968 (22) indicate that the cities of Birmingham, Alabama; Covington, Kentucky; Detroit, Michigan; Cincinnati and Youngstown, Ohio; Allentown, Bethlehem, Philadelphia, and Reading, Pennsylvania; Chatanooga, Knoxville, and Memphis, Tennessee; and Charleston, West Virginia already have the $0.2 \mu\text{g}/\text{m}^3$ concentration of Mn in the air.

Toxicity of Methylcyclopentadienylmanganese Tricarbonyl and Cyclopentadienylmanganese Tricarbonyl

Both of these manganese compounds have been used as antiknocks, and both belong to the so-called "sandwich" compounds and are structurally similar to ferrocene. The toxicity of cyclopentadienylmanganese tricarbonyl (CMT) has been studied extensively in Russia by Arkhipova et al. (23-25) because CMT was suggested as a replacement for TEL. Inhalation studies with CMT on rats showed that vapor concentrations of tenths of a milligram per liter in air were lethal with a one-time exposure. Acute inhalation studies with rats using concentrations of $120 \text{ mg CMT}/\text{m}^3$ showed vascular changes such as increased permeability of vessels, edema and hemorrhages and falling blood pressure. Other manifestations of acute poisoning from inhalation of CMT were atrophic changes in the nerve cells, lowering of osmotic pressure of erythrocytes, and hypoxia, an effect caused by molecules of CMT as a whole. Chronic inhalation exposure of rats to CMT at average concentrations of $1 \text{ mg}/\text{m}^3$ produced poisoning caused by accumulation of the substance in the organism. Toxicity to the test animals was characterized by renal and nervous system damage, and by decreased resistance to infection. It was concluded that the chronic toxicity of CMT was polytropic and was related to the metabolic decomposition of this compound to

give small quantities of carbon monoxide, and inorganic forms of manganese. The oral LD_{50} toxicity for CMT was $80 \text{ mg}/\text{kg}$ body weight in white rats, and $3.2 \text{ mg}/\text{kg}$ body weight in mice (24). The structurally similar compound methylcyclopentadienyl manganese tricarbonyl had an oral LD_{50} toxicity of $56 \text{ mg}/\text{kg}$ body weight in mice (26).

Chronic exposure to this compound would be an occupation health problem to people involved in manufacturing the additive and to gasoline attendants who would be involved in gasoline distribution. It could become a health problem to the general public, however, because of the increase in popularity of self-service gasoline stations.

Toxicity of Exhaust Products of Manganese Additive

Exposure to high levels of manganese oxide dusts by manganese ore miners in Chile, Brazil, Morocco, and South Africa, manganese steel workers in Pennsylvania, and manganese workers in dry battery plants in Egypt and Great Britain have shown a high incidence of a neurological disorder similar to Parkinsonism, and a respiratory disease similar to acute lobar pneumonia (27-37). In both these diseases, manganese oxide dust particles in the air of exposed workers, ranged between $5 \text{ mg}/\text{m}^3$ and $60 \text{ mg}/\text{m}^3$. In many instances, the particle size of more than 50% of the manganese oxides was less than 1μ .

Both manganese poisoning and manganic pneumonitis represent diseases which result from excess manganese intake primarily via inhalation and ingestion (27). Manganese, however, is an essential nutritional element in man's diet and has a vital biochemical function as a cofactor in many enzyme systems (38). The concentration of manganese in body tissues is steady, and fairly characteristic of each organ. Manganese levels in grains are substantial since it is a vital component of plant growth. In plants, manganese activates enzymes which catalyze various stages of plant respiration. In soils in the northeastern U.S., manganese concentration may be present in concentrations of $1 \text{ g}/\text{m}^3$ of soil (39). In plants, it is believed that

manganese occurs in a chelated form. This situation would alter the availability of manganese in this coordinated complex form with the strictly inorganic form of manganese in manganese oxide dust (37).

In the body, the highest concentration of manganese is in the bone (an average of 3.5 mg/g of bone weight). The next highest manganese concentration in the body occurs in the glandular tissues, and the liver is considered to be a storage site of manganese. Lung, blood, and blood-forming tissue appear to have relatively low manganese concentrations. It is believed that manganese concentrations in body organs and tissues are homeostatically controlled, but the specific hormonal mechanisms have not been defined (38, 40, 41).

The major portal of entry of manganese in the air is the lung. From studies with radioactive manganese tracers, however, evidence suggests that the bulk of inhaled manganese becomes transferred to the gastrointestinal tract from which it is either absorbed or eliminated (27). The precise sites of gastrointestinal absorption of manganese are unknown, but in studies with inorganic supplements, it appears that the amount absorbed is proportional to the amount supplied for absorption. It has been suggested that gastrointestinal absorption of manganese from the lung is pertinent to the pathogenesis of chronic manganese poisoning (38).

Manganese is primarily excreted in the feces via the bile. The gastrointestinal contents are therefore both the source and sink for manganese. It has been shown that manganese in the bile is probably reabsorbed so that the metal is recycled several times through body tissues before elimination. The rate of manganese elimination is insensitive to the presence of other metals or changes in acid-base balance, but sensitive to the body load. In supplement studies with inorganic manganese, 40–70% of the total dose is eliminated initially in the feces (38).

The dynamics of transport and turnover of manganese in body organs is different for each organ and may suggest how excess manganese intake results in manganese poisoning. Therefore, the partition of manganese varies greatly and is a function of the equilibration dynamics of each organ. Manganese, however,

shows a distinct preference to accumulate in mitochondria rich tissues (38). In studies with ^{54}Mn (27, 40, 42) it was shown that the rate of loss of metal from blood was rapid and correlated well with the rate of uptake by the liver. The transport pathway of manganese in human plasma has been shown to be a β_1 -globulin, rather than transferrin, the transport protein for iron. Manganese has a long residence time in the body after it has gained entry. The turnover rate of manganese by the central nervous system, endocrine glands, and muscle tissue initially is rapid, but with time appears to level off to constant levels which are not discharged readily.

One of the diseases which results from exposure of manganese ore miners to high atmospheric levels of manganese oxide dust is manganic pneumonitis. There was a particularly high incidence of this respiratory disease during the winter of 1939–40 in Moroccan manganese ore miners, with an associated high death rate (33). Reported cases of manganic pneumonitis averaged 65 per 1000 miners. A comparable outbreak of this disease occurred in the winter of 1947. Associated with these outbreaks were deplorable situations of nutrition, housing, and personal hygiene among the miners. It was concluded that manganese was not the sole etiological factor at work, but was certainly an aggravating factor.

Clinical signs of manganese pneumonitis are first those of acute alveolar inflammation (32–34, 37). Breathing is markedly labored and difficult, respiration shallow and gasping. Cough and expectoration are rare. The illness alters, however, after the third day from frank pneumonia to less well defined localization and discrete pleural involvement. Fatality can ensue from heart failure between the fifth and tenth day. Fatality can also occur suddenly in patients considered cured. Sulfonamides and antibiotics have very little effect on the disease. Among patients is observed a condition of leucopenia with relative polynucleosis, an enormous rise in erythrocyte sedimentation rate (120 in the first hour using a Westergren tube), and eosinophilia in the sputum. After observing these clinical manifestations of the disease, it was difficult to determine whether the patient was suffering from an ordinary pulmonary infection com-

plicated and aggravated by manganese, or sub-acute edema, the pulmonary manifestation of a toxic state.

The other disease resulting from an excess respiratory intake of manganese oxide dust is chronic manganism or manganese poisoning. The major oxide of manganese found in manganese ore is manganese dioxide, MnO_2 . Those who contract manganese poisoning exhibit a self-limiting psychiatric disorder, at the end of which permanent neurological manifestations appear and persist even after excess metal becomes cleared from body tissues. Again, the concentrations of manganese in the air were between 4 and 60 mg/m³, a situation which is four orders of magnitude greater than was found in U.S. city atmospheres in 1968.

The neurological syndrome of chronic manganism has three stages (27, 30, 33, 37, 38). The prodromal period is characterized by subjective disorders such as general asthenia and anorexia, staggering gait, times of incoherent speech, periods of aggressiveness, general indifference, lumbar pain and cramps, and periods of insomnia. The intermediate phase is characterized by the development of more objective symptoms. There are more acute disturbances of speech, the assumption of a facial expression which is jovial and fixed and gives the patient a dazed appearance. Spasmodic laughter and weeping, increased clumsiness in movements especially in upper limbs, and hyperemotionalism are characteristic clinical signs of the intermediate phase of manganese poisoning. Walking backward is more difficult and may be accompanied by retropulsion and loss of balance. The established phase becomes readily apparent after 2–3 months. The essential symptom dominating the clinical picture is muscular hypertonia in extension. This is marked by increased muscular rigidity in the lower limbs and face. Movement is difficult and characterized by a "slapping" gate. Lifting weight is impossible and a slight push from the front can topple the patient backward. Along with the muscular rigidity are either spontaneous tremors, or tremors brought on by fatigue, emotion or cold. The fixed facial expression is more pronounced and facial emotion in speech is lacking completely. Spasmodic laughter is more frequent.

Susceptibility of individual exposed workers to chronic manganism in either manganese mining personnel or workers in industrial operations which use manganese metals or oxides, is unpredictable. The latent period of the disease can vary from 18 months to 20 years and the most susceptible age is difficult to determine (27). However, in studies with ⁵⁴Mn, the total body turnover of manganese by healthy exposed miners was twice as rapid as by miners with manganese poisoning. In these same studies, blood levels of manganese in healthy exposed miners was twice as high as in miners with manganese poisoning. This confirms the individual nature of the disease and how some individuals who were exposed to the same atmospheric concentrations of manganese as those patients who contracted manganese poisoning, have the ability to rapidly remove the excess metal from their body tissues. Recently, modification of chronic manganism has been achieved by gradually increasing doses of L-dopa, up to 8 mg/day, for patients with hypokinetic forms of this disease, and 5-hydroxytryptophane, 3 g/day (43, 44). These drugs were used because of the similarity of manganese poisoning with Parkinson's disease.

Consequences of Manganese Exhaust Products and Emission Control Devices

One of the more important questions to be answered in determining the potential health hazard from this replacement for TEL is what effect will manganese exhaust products have on the catalytic muffler emission control devices for both 1975 and 1976. Because there is no legal ban on manganese gasoline additives, this compound may be used in gasoline as an antiknock additive.

Presently, it is not possible to assess the impact of manganese oxides on this catalyst system. Because manganese oxides are such effective oxidation catalysts, their presence may actually enhance the effectiveness of the emission control system. On the other hand, even if hydrocarbons, CO, and nitrogen oxide emissions are reduced, not all of the manganese oxides can accumulate indefinitely in the exhaust emission control system and will be discharged as par-

ticulates, probably as oxides, nitrates, and carbonates. The fact that manganese oxides can catalyze the conversion of sulfur to SO_3 is another important aspect of this possible alternative for TEL. In attempting to assess the possible levels of atmospheric manganese due to a complete switch from leaded gasoline to this manganese antiknock, use has been made of atmospheric lead levels from 1968 EPA air quality data (22), and Ethyl Corporation's projected use level of Mn/gal of gasoline. Atmospheric lead above cities is about $2 \mu\text{g}/\text{m}^3$ for a yearly average. The use level of manganese/gal would be about 1/6 of present Pb levels of gasoline. If it is assumed that lead in the air comes primarily as a result of the use of leaded gasoline, and that the previously leaded gasoline will now be manganese gasoline, then the increase in atmospheric manganese would be $0.35 \mu\text{g}/\text{m}^3$ to give a total yearly average of about $1.2\text{--}1.5 \mu\text{g}/\text{m}^3$.

The levels of atmospheric manganese found in connection with the incidence of manganic pneumonitis and chronic manganese poisoning were $5\text{--}60 \text{ mg}/\text{m}^3$, on the average. These same studies on diseases from excess manganese exposure also showed that ambient weather conditions greatly influenced the manganese concentration in the air. Foggy weather with no wind could easily increase the atmospheric concentration of manganese to $10\text{--}20$ times the average. In this respect, people caught in traffic jams and inner city dwellers could very possibly be exposed to higher levels of manganese oxides in the air than a yearly national average would show. In assessing the potential health hazard from this antiknock compound, consideration of the individual susceptibility of this disease and the difference in turnover and body loads of Mn must be taken into account. Using the Air Quality Data for 1968 from the EPA illustrates that atmospheric concentrations of manganese could be about $1 \mu\text{g}/\text{m}^3$ as compared with $5\text{--}60 \text{ mg}/\text{m}^3$ concentrations of manganese oxides associated with the incidence of manganese poisoning and manganese pneumonitis. The threshold limit value (TLV) for manganese set by the American Conference of Government Industrial Hygienists in 1968 is a ceiling value of $5 \text{ mg}/\text{m}^3$. It must be remembered that this value is for usually strong healthy workers who do not work

in this atmosphere all the time, and who may be moved from jobs with high manganese levels in the air, at regular intervals. Whether the general population can tolerate chronic exposure to higher projected atmospheric levels of manganese and higher levels of sulfates as a result of this manganese antiknock additive is a question which should be given serious consideration while there is still time to do so.

Conclusions

The controversy on banning lead from gasoline and the projected use of catalytic mufflers to achieve the standards of the Clean Air Act of 1970 has degenerated to a crisis situation complete with uncompromising positions on the issues. This situation is due in part to the inability to answer fundamental aspects about this question and the use of correlations between exposure levels to lead and disease which are difficult to substantiate. It is this kind of atmosphere which has stifled critical discussion and analysis of the economics and health effects of the methods proposed to meet these standards. This is an important discussion because the alternatives are backed by interest groups which would be most affected economically by the outcome. The inclusion of economics into a discussion on the alternatives to a problem historically has added to the general confusion of the issues and resulted in oversimplified or wrong selection of an alternative which is expedient, but may not solve the root problem, and even may add to it. With respect to size and influence, the two interest groups involved in the alternatives for leaded gasoline are not evenly matched. Indeed, it appears that the proposed alternative will be the use of higher weight percentages of aromatics to achieve comparable octane boosting and antiknock capacity as TEL, coupled with the use of the dual catalytic converter system to clean up the exhaust.

These are alternatives which partially solve the exhaust emissions problems but do not consider some of the fundamental aspects of not only the pollution problem, but also the increased utilization of metallic and petroleum resources problem. Two of the root problems are the design of the internal combustion engine

and the composition of gasoline used. Until the air pollution crisis from automotive exhaust erupted, automobile engines were being designed for higher and higher performance. The achievement of this purpose manifested itself in shorter stroke engines, higher compression ratios, and the use of richer fuel mixtures. Exhaust emission control regulations resulted in modifications of engine design to meet these standards. Changes in engine design to solve pollution problems have to be evolutionary and cannot occur immediately. However, complete engine redesign must occur simultaneously and would appear to attack the root problem in a more reasonable and acceptable manner. The modification of engines with more sophisticated emission control devices rapidly reaches the point of diminishing returns, as far as reducing the rate of utilization of fossil fuels and the enhanced onset of the energy crisis are concerned. This is due to the fact that more horsepower is diverted from running the engine to running the control devices. Therefore, more gasoline is required to travel the same distance, and the emission control devices must handle a larger volume of exhaust emissions. Compounding this problem still further, the National Academy of Sciences (45) raised serious doubts about not only the performance of these catalyst systems in actual use, but also the ability of maintenance personnel to properly repair these systems.

The pollution problem from the automobile exhaust is an engineering problem, and always has been. The redesign of the internal combustion engine must be accompanied with a simultaneous redesign of gasoline composition. These design changes are a tremendous challenge since the automotive engineer must operate now within efficiency, environmental, fuel supply, and economic constraints.

With respect to engine design, the stratified-charge CVCC (complex vortex controlled combustion) engine by Honda (46), may be in the right direction. The operation of this engine initially involves ignition of a small amount of a very rich mixture in a small chamber above the main cylinder body. The flame then spreads to a larger quantity of a very lean mixture in the larger main cylinder and completes the work of combustion with the downward stroke of the piston. This design has the effect of not allowing

cylinder gas temperatures to reach the higher temperatures (2900°F range) required for significant formation of nitrogen oxides. The use of lean mixtures in the larger chamber has already cut down on the quantities of CO and hydrocarbons produced so that the engine can achieve the 1975 U.S. Standards for Exhaust Emissions without control devices. The average results with a 1955-cc 4-cylinder CVCC engine compared with U.S. Standards are shown in Table 16.

Table 16. Comparison of emissions from CVCC engine with 1975 U.S. standard.

	Emissions from Honda engine, g/mi	Emissions 1975 U.S. Standards, g/mi
HC	0.23	0.41
CO	2.41	3.40
NO _x	0.95	3.00

This design was achieved without loss of performance (9.1 compression ratio 72 mm bore, and 88 mm stroke), and without drastic changes to present engine block design such as the Wankel engine would be. The developments by Honda require watching and more complete analysis than can be given here to determine whether or not the CVCC engine completely solves the air pollution problem.

It can be seen that the methods used to achieve the standards of the Clean Air Act have affected many industrial endeavors which at first may not have appeared to have any connection at all with these proposed alternatives. However, it is hoped that discussion of these proposed alternatives and control devices has been stimulated so that they may be given due consideration for their impact on environmental health.

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